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Valorization of bark for chemicals and materials: A review

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ABSTRACT

The annual bark yield in Canada is as much as 17 million m^3. Currently, more than half of the bark is incinerated or landfilled and the remainder of the bark is mainly used as a cheap source of energy in saw/pulp mills. Both bark incineration and landfilling can lead to environmental problems. Due to the abundance of ash in bark and the lower sintering point of bark ash than that of wood ash, the combustion of bark can lead to fouling which would damage the combustors. Bark contains a large fraction of extractives and lignin (up to 50 wt% on a dry basis), which can be utilized as a renewable source of chemicals, particularly aromatic chemicals. The technical routes and technologies on the valorization of tree barks for chemicals and materials are reviewed in this paper. These include direct utilization of bark for wooden panels, and extraction for extractives (mainly tannin) and their the application in resins and foam materials, as well as conversion of bark via thermochemical technologies, mainly phenolysis, direct liquefaction in alcohols and pyrolysis. Finally, some challenges and perspectives on the production of chemicals and materials from bark are discussed.

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1. Introduction

Currently, chemicals and energy are mainly derived from fossil fuels, which is challenged by the rapidly declined reserves and fluctuating prices of crude oil. Thus, research into alternative

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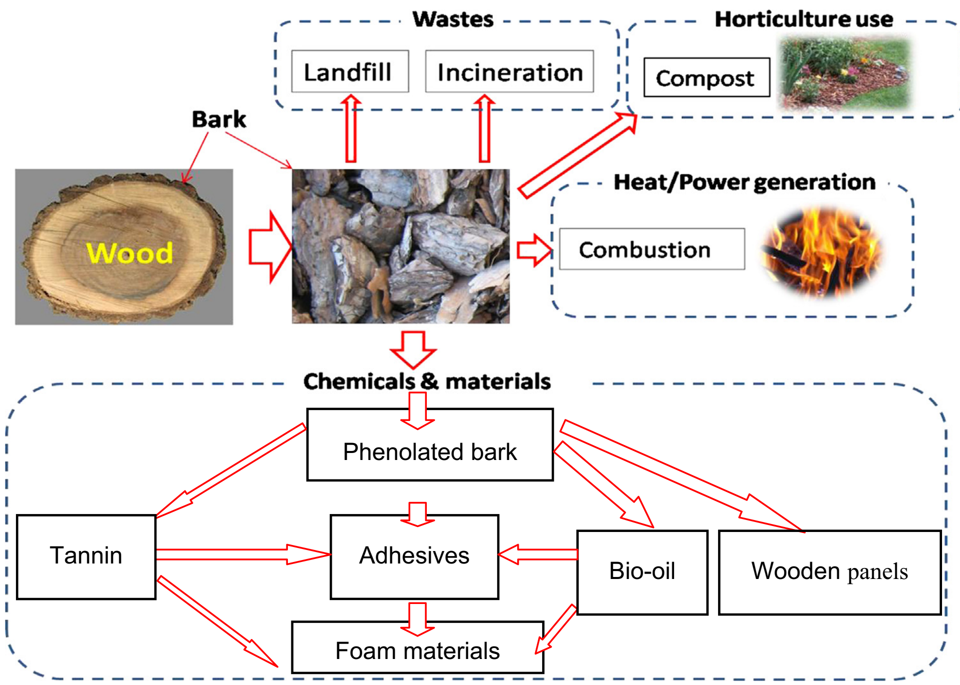


Fig. 1. Valorizations of tree barks.

sources for chemical and fuel production has attracted a great deal of attention. Biomass is mainly composed of cellulose, hemicellulose and lignin, as well as a small amount of extractives and ash. Through thermochemical and biochemical processes, biomass has the potential to provide value-added chemicals, such as reducing sugars, furfural, ethanol and other products. Bark, which is defined as all the tissues external to and surrounding the vascular cambium, comprises about 9–15% of a typical log by volume or 13–21% on a dry weight basis [1,2]. The annual bark yield in North America, mainly derived from pulp and wood industries, is estimated to be more than 50 million tons [3], among which around 17 million m^3 is produced in Canada [4]. Currently, bark is mainly used as an energy source by direct combustion in sawmills and pulp mills, or as compost for horticulture use. In the U.S., thermal energy production absorbs about 83% of softwood bark and 66–71% of hardwood bark, and the market share of bark for horticulture use is about 15% of softwood bark and 30% of hardwood bark [5]. In Canada, only a fraction of the bark is used for thermal energy production, and more than half of the bark is incinerated or landfilled as waste [4]. Compared with coal, bark's heating value is normally lower, 10 t of completely dry bark has a gross average heating value equivalent to that of 7 t of bituminous coal, but bark has negligible sulfur, which means bark combustion results in much less pollution to the environment [6]. Ash is the noncombustible part in bark and a high ash content tends to lower the heating values, while bark generally contains less volatile matters and a higher percentage of fixed carbon than wood [7], resulting in bark's higher caloric values than wood. It has been reported that the presence of resinous extractives in bark would contribute to increase in bark's heating values [8]. For example, Resch's research [9] showed that resin free bark pellets had higher heating values (HHV) of 17.2–22.8 MJ/kg while resinous bark had an HHV of 20.4–25.1 MJ/kg. Another advantage is that resinous bark pellets show better mechanical properties, so that the pellets are more durable [10].

However, bark's caloric value is still much lower than that of fossil fuel [11,12], and due to the abundance of ash in bark and the lower sintering point of bark ash than that of wood ash, bark combustion can lead to fouling which would damage the combustors. Thus, direct combustion of bark for energy recovery is not that economically advantageous. Studies have been conducted on various new applications of wood bark as pollutant absorbents [13–15], filler for phenolic resins when applied in plywood [16], metal ion or formaldehyde absorbers [12,17], and proanthocyanidin with antioxidant activity [18], etc. However, bark valorization is still challenging due to its heterogeneous structure, diverse chemical composition, low strength and dark color.

Bark is not either a favorable feedstock for the production of fermentable sugars due to the fact that it contains a higher content of lipophilic extractives, and aromatic compounds including tannin and lignin [19,20]. The presence of bark in the wood pretreatment processes necessary for sugar production decreases the recovery of sugars, furfural and 5-hydroxymethylfurfural in the pre-hydrolysate. Pre-hydrolysate resulting from the processing of bark-containing wood exhibits poorer fermentability into ethanol than that from the bark-free wood [21,22]. In contrast, the aromatic polyol structure components in bark favor its utilization in phenol formaldehyde (PF) resins and foam production. Valorizations of bark including utilization of bark in the production of chemicals and materials, e.g., wooden panels, tannin, resins and foams, bio-oils, etc., are summarized in Fig. 1.

Although barks have been widely used for medicine, dyes, spices, incense or phytotherapy, cork, animal bedding and absorption for pollutants, this review focuses on bark utilization for chemicals and materials, specifically for the production of wooden panels, tannin, resins and foams, as well as the thermochemical conversion of bark (via phenolysis, direct liquefaction, and pyrolysis), and the applications of bark thermochemical conversion products.

2. Chemical compositions of tree bark

Bark refers to all tissues external to and surrounding the vascular cambium. It can be divided into the inner bark and outer bark. Inner bark, the region of bark nearest to wood, is composed mainly of secondary phloem extending from the vascular cambium to the innermost or last-formed layer of periderm, and

Table 1
Chemical composition of wood and bark.

Species			Components [a]/%					Ref.
			Lignin	Holo-cellulose	Extractive[b]	Ash	1% NaOH solubles	
Softwood	Cedar	Sapwood	28.71	72.24	6.89	0.73	13.89	[27]
		Heartwood	27.14	67.55	9.00	0.45	19.50	
		Inner bark	28.29	64.14	10.69	4.43	34.23	
		Outer bark	33.14	58.50	13.07	6.01	45.16	
	Karamatsu	Wood	22.5	69.5	0.9	0.2	-	[34,35]
		Bark	26.7	82.4	1.1	0.2	16.6	
	Akamatsu	Wood	23.5	71.5	1.1	0.3	-	
		Bark	27.3	83	1.3	0.3	14.7	
	Radiata Pine	Wood	24.8	61.6	6.5	0.2	-	
		Bark	31.5	78.1	8.3	0.3	23.6	
Hardwood	Udaikanba	Wood	20.7	75.8	1	0.2	-	
		Bark	22.9	83.7	1.1	0.2	17.9	
	Buna	Wood	22.4	73.6	0.9	0.4	-	
		Bark	25.7	84.3	1	0.5	16.5	
	Mizunara	Wood	20.5	73.3	0.8	0.4	-	
		Bark	23.1	82.5	0.9	0.5	19.7	
	Endemic oak	Sapwood	24.93	66.41	–	0.72	20.74	[33]
		Heartwood	25.51	66.24	–	0.44	23.3	
		Bark	30.82	50.59	–	13.5	37.47	

[a] Calculated based on dry basis if the original data was based on extracted base.
[b] Extractives were obtained by ethanol–benzene extraction.

usually contains several seasons' growth. The inner bark is also called "active bark" because it is still living. The outer bark is the dead part of the bark, being the region from the last-formed periderm on the attached outermost surface, composed of old phloem and periderm that can be subdivided into phellogen, phellem or cork, and phelloderm [23,24]. Even though there are some obvious distinctive characteristics of inner and outer barks, separation of them is expensive and not practically meaningful. They are thus more commonly utilized together as whole bark.

Bark differs from wood in terms of chemical compositions. Generally, bark consists of polysaccharides (cellulose, hemicelluloses), pectic substances, phenolic polymers including lignin and high molecular weight tannins, and cross-linked polyesters such as suberin and cutin. The holocellulose in bark generally contains a higher proportion of mannose and the lignin in some conifer barks can be more highly crosslinked than wood lignin. In addition, some low molecular weight components such as low molecular weight phenolics, fatty acids and resins can also be found in bark [25]. The chemical composition of bark varies with tree species (hardwood or softwood), tree parts (root, stem or branch), tree stress (normal wood, tension wood or compression wood), tree parts (root, stem or branch), geographic location, climate and soil conditions. As summarized in Table 1, the lignin content of the bark of a tree is usually higher than that of the wood, depending on the wood species. Compared with wood, bark contains much more extractives and ash. Most of the extractives in bark are found to be similar to those contained in the wood, and the main difference is that many barks contain more polyphenols and suberin of a high molecular weight [26–28]. Lignin in inner bark is claimed to be similar to the corresponding wood lignin while the outer bark lignin differs from the inner bark lignin [29], and the fractions of specific functional groups in bark lignin also differs from those of the wood lignin. For example, Caribbean pine bark lignin contains more carboxyl and phenolic hydroxyl groups but fewer methoxyl groups than wood lignin [30].

Bark extractives, especially suberin and tannins, can be generally extracted with 1% aqueous NaOH solution at 70–90 °C. The extracted residue can be used for the quantitative determination of acid insoluble lignin using sulfuric acid hydrolysis [31]. However, one problem with this method is that a large fraction of the pectins and hemicellulose can also be removed during the extraction in alkaline solution, which leads to some inaccuracy in bark component determination [32]. Ash is the inorganic residue remaining after combustion, which mainly contains metal oxides (K_2O, MgO, Na_2O, CaO, and Fe_2O_3, etc.), windborne soil or sand particles [33].

3. Bark-based wooden panels

Since the 1970s, bark-based panels bonded using urea formaldehyde (UF) resin have been extensively investigated. In a study by Pedieu et al. [36], white birch inner bark particles were applied in the core layer of particleboard with wood fiber-reinforced surfaces, where up to 70% of wood fibers could be replaced by white birch inner bark while maintaining the required mechanical and physical properties. Panels made of 25% wood fiber in the surface layers and 9% wood fiber in the core layers exhibited the best mechanical properties. Bark panels containing 22% and 5% wood fibers in the surface layer and core layers, respectively, were preferred if linear expansion is of concern. In another study by the same group, white birch outer bark was used in the surface layers while coarse wood particles were used in the core layers. It was found that panels could be formed with up to 45% white birch outer substitution of wood particles without sacrificing the required mechanical and physical properties [37]. Black locust (*Robinia pseudoacacia* L.) wood particleboard containing mimosa bark in a core layer was also manufactured [38]. Bark in the core layer was found to significantly decrease formaldehyde emission and thickness swelling of particleboards. However, due to the low wettability and porous structure of the bark, the modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond strength (IB) of the bark-containing particleboards decreased with the increasing bark substitution. It was demonstrated that at bark addition levels greater than 12.25%, the mechanical strength, formaldehyde release as well as the thickness swell deteriorated significantly. Muszynski and McNatt [39] systematically investigated UF adhesive bonded wooden boards in which wood was substituted by bark in the range of 0–100 wt%. The characteristic indices of MOE, bending strength, tensile strength, compressive strength, internal bond strength, shear strength, hardness, nail withdrawal resistance, screw withdrawal resistance, dowel

withdrawal resistance were all found to decrease with increasing bark content in the particleboards. However, the physical and mechanical properties of the boards could still meet the requirements for furniture manufacture with up to 30% bark substitution. In addition to synthetic adhesives (UF resins), other interesting chemicals such as citric acid were proven to favor the bonding of bark particles. *Acacia manugium* bark was molded with citric acid powder (20 wt%) at 180 °C and 4.0 MPa for 10 min. The resulting molding's modulus of rupture (MOR) and modulus of elasticity (MOE) values can reach 18.1 MPa and 4.9 GPa, and did not decompose during a repeated water boiling treatment due to the formation of ester linkages between the carboxyl groups in citric acid and the hydroxyl groups in the bark, which could also account for its excellent bonding strength [40].

In addition, bark based wooden panels can be produced through self-bonding, which is mainly based on plasticization, physical consolidation, and polymerization of the extractives within the bark particles. Below 200 °C, physical properties are responsible for bark softening while above this temperature, polymerization and partial degradation of bark components mainly contribute to the bonding [41]. Higher temperatures favor the bonding of bark in panels: MOR and internal bonding strength (IB) of self-bonded bark particleboard panels pressed at 230 °C are respectively 9 times and 3 times higher than those of the panels pressed at 170 °C. Fine or mixed-size of bark particles and higher pressing temperatures leads to denser packing, thus improves the mechanical properties such as MOE, MOR. MOR and IB strength of the self-bonded particleboard panels with mountain pine beetle-infested lodgepole pine bark [42]. Gao et al. [43] made panels with three different bark contents without any adhesive: the first type of panels was made exclusively with bark, the second was homogeneous structure panels made with 30 wt% wood fiber and 70 wt% bark fiber, the third was a sandwich structure with 30 wt% black spruce wood fiber in the two face layers and 70 wt% steam-treated bark fibers in the core layer. It was found all of the bark fiberboards, produced without any synthetic adhesive met the requirements of 115-grade fiberboard panels according to the ANSI A208.2 (2009) standard as far as IB, MOR, MOE and flexural properties were concerned. Even though lots of studies of bark based wooden panels have been conducted so far, bark panels are not commercially available due to their deteriorated appearance, inferior performance in other physical tests (large linear expansion and thickness swell), as well as the extremely high temperatures and long press times needed for the panel production resulting from the poor thermal conductivity of bark [44]. One way to overcome these problems to some extent is to pre-treat bark, by steaming or alkali treatment for example. Steaming treatment of bark is proposed to lower the required pressing temperature and shorten the pressing time for panel manufacture [45]. Both steam retention time and pressure during steaming black spruce bark have a significant effect on MOE and MOR of medium density fiberboard, and steam pressure is found to be a significant factor for IB. Neither steam retention time nor steam pressure significantly influences thickness swell, water absorption or linear expansion [46]. And increased steam pressure can shorten the fiber length, deteriorate the strength and elastic properties and long-term swelling properties of bark panels [45].

Another way to pre-treat bark is by alkali treatment. The effects of alkali pretreatment of bark on bark-based panels were found to strongly depend on bark species. For spruce bark, alkali pretreatment improved the mechanical and physical properties of bark based panels [47], but for white birch outer bark, it negatively affected the mechanical and physical properties of the finished panels [36,48]. The combination of alkali treatment and steaming improved both the mechanical properties and physical properties like color. Geng et al. [47] soaked spruce bark in 1% sodium hydroxide solution at room temperature for 1 min, drained for 10 min, then steam-treated the bark for 3 min at 0.3 MPa or 0.75 MPa. The treated spruce bark was then used for producing panel by pressing at 210 °C for 6 min. The results showed that besides having a lighter color, the combined treatment of bark improved both mechanical properties and physical properties of the resulting panels. Specifically, IB, MOR, MOE increased from 0.49, 10.8 and 16.43 MPa to 1.97, 17.2 and 32.5 MPa, respectively, while thick swelling of the fiberboard decreased slightly from 29.8 to 28.6%. In addition to bark based panels, bark plastic composites have also been produced and studied [49]. Extruded black spruce bark-polyethylene composite exhibited a higher strength, but greater brittleness than aspen bark-polyethylene composite [49].

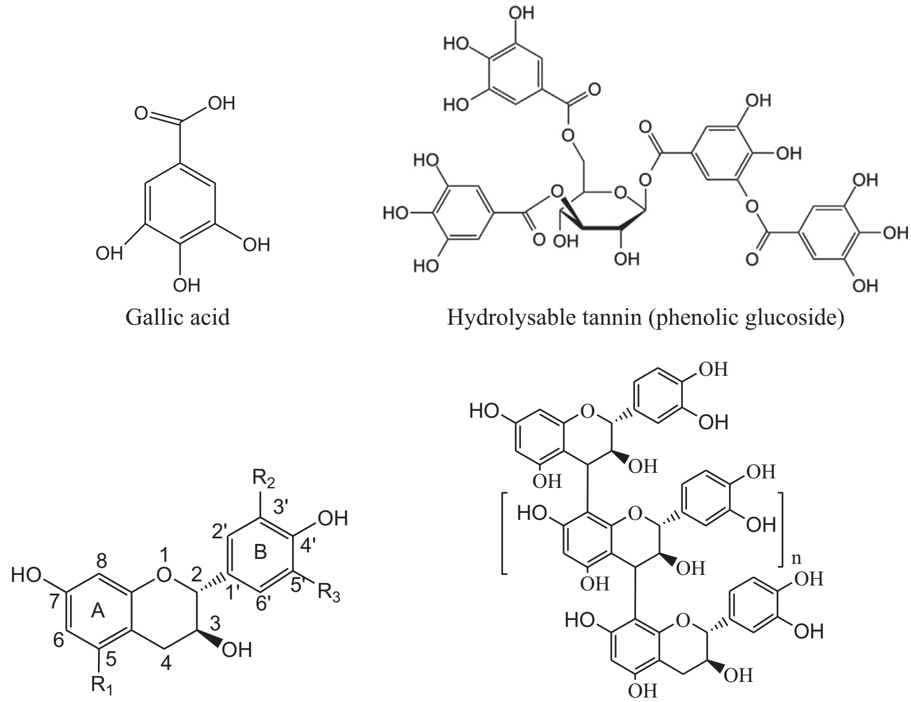
4. Bark tannin extractive and its applications

4.1. Tannin chemistry and extraction from bark

Due to the abundance of extractives in bark, full valorization of bark always requires extractive recovery and application. Tannins as the main components in bark extractives, are naturally occurring polyphenolic compounds and have been traditionally used in leather industry due to their high reactivity with protein in animal skin. Tannins are categorized into gallotannin, ellagitannin, condensed tannin and complex tannin. The former two can be hydrolyzed by acid into gallic acid and ellagic acid, respectively, and are thus called hydrolysable tannins; condensed tannins are oligomeric and polymeric proanthocyanidins consisting of coupled flavan-3-ol (catechin) units; while complex tannin contains both a gallotannin unit or an ellagitannin unit, and a catechin unit [50]. In general, tannins are just divided into hydrolysable tannins and condensed tannins. Hydrolyzable tannins are derivatives of gallic acid (3,4,5-trihydroxyl benzoic acid), which are simple mixtures of pyrogallols, gallic acid, ellogic acid, and esters of glucose with gallic or digllic acids [51–53]. Typical hydrolyzable tannin structures (both hydrolysable and condensed) are shown in Fig. 2. Condensed tannins contain complex chemical structures of polyphenolic compounds comprising groups of polyhydroxyflavan-3-ol oligomers and polymers linked by carbon–carbon bonds between flavonol subunits. They have high reactivity to chemicals such as formaldehyde and constitute more than 90% of the total tannin production in the world [54,55]. The structure of condensed tannins varies with bark species. Condensed tannins from Acacia bark are predominantly constituted of 4–6 bonded flavonoid units, while tannin from pine bark or western hemlock bark contains 4–8 boned flavonoid units that are catechin type [56]. The 4–8 linked interflavanoids are thought to be linear flavonoid polymers, while 4–6 linked interflavanoids are polyflavanoids of more globular and possibly branched.

The main commercial sources for condensed tannins are quebracho (*Schinopsis balansae*) wood and the barks of wattle (*Acacia mearnsii*) and chestnut (*Castanea Sativa*) [56,57]. Condensed tannin content in extractives is usually measured by the Stiasny number (value). A higher Stiasny number means more condensed tannin in the extractives. Stiasny number is in general determined by the Stiasny precipitation method, which is based on the reaction of tannin and formaldehyde in the presence of hydrochloric acid to form insoluble high molecular weight condensation products, which is also a common method to characterize bark extractives for tannin and phenolic contents [58]. Tannin is so far the only commercialized highly valuable chemical product from bark.

The yield of tannin from bark depends on species [60], age, parts of the tree [61–63], storage time after tree felling [64], and extraction method [65]. Before extraction, bark is generally air dried or dried at comparatively low temperatures (≤40 °C) to avoid the possible self-condensation of the extractives and the formation



R_1=R_2=R_3=H	Progibourtinidin
R_1=H, R_2=R_3=OH	Resorcinol
R_1=OH, R_2=R_3=H	Propelargonidin
R_1=R_2=OH, R_3=H	Procyanidin
R_1=R_3=H, R_2=OH	Profisetinidin
R_1=R_3=OH, R_2=H	Catechin
R_1=R_2=OH, R_3=H	Phloroglucinolic
R_1=R_2=R_3=OH	Prodelphinidin

Condensed tannin

Fig. 2. Schemes of tannin precursors and the corresponding tannin structure .
source: modified from Porter [59]

of bonds between the extractives and fiber or protein leading to low extractability of tannins from the bark. Generally, the bark of older trees gives higher tannin and extractive content [62]. The outer bark of some conifers contains the biggest percent of extractable total phenols, followed by inner bark, heartwood, and sapwood. So far, no single extraction method is able to extract pure tannin even though some of the extraction processes result in extractives with a Stiasny number as high as 90%, as shown in Table 2.

Traditionally, tannins are extracted with water [69]. Water extraction at a lower temperature results in a lower extractive yield but a higher tannin content [70,71]. Extractives obtained through hot water extraction contain hemicellulose, some acetic acid and even lignin [72]. Smaller bark particle size also increases extractive yields due to improved mass transfer. It is interesting to note that the amount of water used during extraction has little influence on the extractive yield [73]. Makino et al. [74] extracted tropical tree barks of *Acacia mangium*, *Acacia auriculiformis*, *Rhizophora apiculata*, and *Larix leptolepis* at the temperatures ranging from 20 to 100 °C for 3 h in water and at room temperature in 70 vol% aqueous acetone, respectively. The results are listed in Table 3. Extraction in water at higher temperature in water extraction led to a higher extractive yield but lower total polyphenolic content. However, Extractive yields at 100 °C for 3 h in water were lower than those obtained by 70 vol% aqueous acetone extraction at room temperature. In terms of total phenolics content in extractives, water extraction at 100 °C performed almost the same as 70 vol% aqueous acetone extraction at room temperature. However, due to hydrolytic degradation of the hemicellulose present at elevated temperature, water extraction at 100 °C resulted in a much higher sugar content than the 70 vol% aqueous acetone extraction. The optimum temperature for water extraction of *A. mangium* and *L. leptolepis* barks to obtain extractives with a low sugar component is approximately 80 °C. Ultrasonic assisted extraction (30 min, 35 kHz) produced similar results to reflux extraction (100 °C for 30 min). Microwave extraction (3 runs of 1 min plus 2 min pause, 35 kHz) resulted in a higher extractive yield than reflux extraction (100 °C for 30 min).

Organic solvents extensively used for tannin extraction include methanol, ethanol and acetone. These solvents can solubilize tannin, and can be easily recovered for recycle by distillation/evaporation. The choice of solvent(s) and the optimized conditions for tannin extraction are bark species dependent. For instance, the optimum extraction conditions with respect to phenolic compound yields for *Pinus pinaster* bark in ethanol were determined at 50 °C for 90 min at the solid–liquid ratio of 1:5 (w/w) [75]. For *A. mangium* bark, however, water is a more suitable for extracting tannin from the bark than acetone or methanol [76]. Co-solvents of water with an organic solvent have been demonstrated to be more efficient in tannin extraction than the component mono-solvents. Derkyi et al. [77] studied aqueous acetone (i.e., acetone–water co-solvents) and aqueous ethanol extraction of tannin from *Pinus caribaea* bark. In 60% aqueous acetone extraction (liquid–solid ratio of 29.8:1), a maximum extractive yield of 17.57% and Stiasny number of 76.96% were obtained at 58 °C for 78.5 min. For aqueous ethanol extraction at 71.5 °C for 79.2 min, with an ethanol

Table 2
Performance of some extraction methods for bark extractives.

Bark species	Conditions	Yield/%	Stiasny number/%	References
Acacia mangium	Lixiviation in aqueous sodium sulfite and sodium carbonate at 75 °C for 3 h	23.30	90.00	[66]
Pinus caribaea	liquid/solid 29.8:1, Lixiviation in 60% aqueous acetone at 58 °C for 78.5 min	17.57	76.96	[67]
	liquid/solid 26.4:1, lixiviation in 21.9% aqueous ethanol at 71.46 °C for 79.2 min	20.68	80.47	
Khaya ivorensis	liquid/solid 15:1, lixiviation in distilled water over night at room temperature, then refluxed for 2 h	27.60	77.50	[68]
Avicennia alba		23.60	72.80	
Pinus oocarpa var. oocarpa	liquid/solid 15:1, refluxed in 5% aqueous Na_2CO_3 for 2 h	43.92	90.48	[51]

Table 3
Extraction of several tropical barks in water [74].

Bark species	Conditions	Yield/%	Total phenolics in extractives/%
Acacia mangium	70 vol% aqueous acetone at room temperature	37.9	46.7
	water at 20 °C	18.4	49.5
	water at 40 °C	19.1	52.9
	water at 60 °C	22.5	52.9
	water at 80 °C	24.5	50.6
	water at 100 °C	27.5	51.6
Acacia auriculiformis	70 vol% aqueous acetone at room temperature	28.6	38.1
	water at 20 °C	18.9	47.1
	water at 40 °C	18.6	51.6
	water at 60 °C	21.5	52.6
	water at 80 °C	23.0	50.9
	water at 100 °C	25.0	51.6
Rhizophora apiculata	70 vol% aqueous acetone at room temperature	20.2	39.6
	water at 20 °C	12.8	50.8
	water at 40 °C	14.9	47.0
	water at 60 °C	15.7	42.0
	water at 80 °C	17.0	38.8
	water at 100 °C	18.4	43.5
Larix leptolepis	70 vol% aqueous acetone at room temperature	11.0	41.8
	water at 20 °C	2.9	72.4
	water at 40 °C	3.0	70.0
	water at 60 °C	5.4	55.6
	water at 80 °C	7.8	50.0
	water at 100 °C	10.7	49.5

concentration of 21.9% and a liquid–solid ratio of 26.4:1, the maximum tannin yield of 17.95% was obtained with a Stiasny number of 88.25%, as summarized in Table 4. Most bark extraction in 70 vol% aqueous acetone or ethanol has been demonstrated to be efficient for phenolics recovery (Table 3) [74,78,79].

In addition to organic solvents, alkaline solutions are used extensively to extract tannin from bark. Alkaline extraction is able to remove extractives including flavonoid oligomers and polymers, waxes, suberin degradation products, polysaccharides and lignin. A higher extractive yield of at the expense of decreased extractive reactivity toward formaldehyde can be obtained when increasing the concentration of NaOH [51,80,81]. Extractive yield obtained by alkaline solutions lixiviation of *P. pinaster* bark was 2.5 to 6 times higher than that obtained through water lixiviation. Temperature and alkali type greatly affect extractive yield: extraction efficiency using Na_2CO_3 is much lower than extraction with NaOH [70,82]. The highest condensable polyphenol content (27.3% of bark) of spray-dried extractives is obtained by extraction at 90 °C in 5% NaOH solution with a solid–liquid ratio of 1/6 [63]. For eucalyptus (*Eucalyptus globulus*) bark extraction in NaOH, Na_2SO_3 and Na_2CO_3, as shown in Table 5, NaOH proved to be the most efficient reagent in terms of extractive yield, followed by NaOH+Na_2SO_3 co-reagents, Na_2CO_3+Na_2SO_3, and Na_2SO_3 alone. The Stiasny number and molecular weights of the extractives decreased with increased concentration of extracting reagent. Increasing extraction temperature from 70 to 90 °C increased both yield and Stiasny number of extractives [83]. In *Pinus radiate* bark extraction, a high extractive yield of around 30% was obtained from a four-stage sequential extraction including the two initial hot water extraction stages followed by a third aqueous NaOH (pH 8.3) extraction stage and a final hot water wash stage. The final yield of extractives was two times of that obtained from the first two stages with hot water extraction alone [84].

Even though hot water, aqueous methanol or acetone, or alkaline solutions can efficiently remove tannin from bark, condensed tannin cannot be completely extracted due to covalent bonds between the condensed tannin and the cellulose matrix [85]. Steam pretreatment followed by solvent extraction seems to be effective in extracting a greater fraction of the condensed tannin from bark. In one study, *A. mearensii* bark was first steamed

Table 4
Optimized conditions for aqueous ethanol extraction of tannin from *Pinus Caribaea* bark [77].

Optimized response	Temp (°C)	Time ($_{min}$)	Solvent conc. (% v/v)	*L–S* ratio (v/wt)	Tannin (%)	Sugar (%)	Stiasny number (%)
Tannin	71.5	79.2	21.90	26.40	**17.95**	5.20	88.25
Sugar	47.4	92.9	47.60	10.90	1.86	**1.93**	74.34
Stiasny number	40.8	134.0	62.80	23.60	4.29	4.52	**88.25**
Tannin, sugar and Stiasny number	52.1	150.0	43.60	10.00	**2.65**	**3.24**	**92.25**

Table 5
Yield and Stiasny number of extractives obtained from Eucalyptus bark in different extraction condition [83].

Bark species	Conditions	Yield/%	Stiasny number/%
Eucalyptus globulus	Water 90 °C	6.80	37.6
	NaOH 2.5%–70 °C	9.81	23.1
	NaOH 2.5%–90 °C	10.38	23.5
	NaOH 10%–70 °C	16.39	14.3
	NaOH 10%–90 °C	18.90	16.5
	Na_2SO_3 2.5%–70 °C	6.80	28.9
	Na_2SO_3 2.5%–90 °C	8.55	35.5
	Na_2SO_3 10%–70 °C	6.81	9.7
	Na_2SO_3 10%–90 °C	10.19	15.3
	NaOH 2.5%–Na_2SO_3 2.5%–70 °C	7.94	8.9
	NaOH 2.5%–Na_2SO_3 2.5%–90 °C	12.30	12.0
	NaOH 5%–Na_2SO_3 5%–70 °C	13.25	5.3
	NaOH 5%–Na_2SO_3 5%–90 °C	16.19	5.2
	Na_2CO_3 2.5%–Na_2SO_3 2.5%–90 °C	10.72	14.3
	Na_2CO_3 5%–Na_2SO_3 5%–90 °C	10.70	5.1

in a stainless steel autoclave and then filtered. The filtrate was then freeze-dried to recover the solid brown extractives. In order to characterize the extractives, the solids were re-dissolved in water and extracted successively with *n*-hexane and ethyl acetate. It was evidenced that under the steam treatment conditions (12.0 g bark, 75 mL water, 140 °C, 30 min), a total phenolics yield of 25.31% was obtained, which is higher than that obtained through boiling water extraction for 3 h (21.7%) [86].

Applications of tannin from bark extractives are however limited due to its low solubility, high viscosity, too high or low reactivity. Sulphitation, which is generally accomplished by adding sodium sulfite into aqueous sodium hydroxide or sodium carbonate for extraction, can change the solubility and viscosity of tannin [87]. As shown in Fig. 3, pyran ring opening during sulphitation of bark tannin may occur [88,89]. The effects of sulphitation on extractive viscosity, acidity and reactivity depend on bark species. For instance, sulphitation of the extractives from the *Pinus halepensis* bark in water or aqueous sodium hydroxide did not influence the viscosity, acidity and reactivity of the extractives. In contrast, sulphitation of the extractives from *Pinus silvestris* and *Picea aaabies* barks increased the viscosity, acidity and reactivity of the extractives [80].

4.2. Tannin utilization for biomaterials

4.2.1. Tannin-based adhesives

Traditionally, tannin is used to transform animal skins and hides into leather. This process is achieved through the reaction between the hydroxyl groups of tannins and the peptide bonds in amino acids present in animal protein. In addition, tannin also has applications in tiles and floor manufacturing, as well as in the drilling muds used in drilling oil wells.

Studies on tannin based adhesives date back to 1950s. Wattle bark tannin based adhesive has been commercially used for exterior-grade particleboard in the Southern hemisphere for forty years [90]. Tannins from the barks of spruce [70,91], pine [56,92–95], Nigerian [65], Taiwan acacia and China fir, etc. [96] have also been extensively applied in preparing tannin adhesives at least in lab scale. In a flavonoid unit of tannin, the nucleophilic centers on A ring tend to be more reactive than those on B ring, and formaldehyde reacts with tannins through the formation of methylene bridge linkages at the reactive positions. All flavonoid A rings tend to react at either position 6 or 8, or in the case of upper terminal flavonoid units, at both positions [97]. As shown in Fig. 4, in a typical reaction, formaldehyde reacts with tannins at position C8 of the resorcinolic A ring to form methylene linkages. Like the reaction between phenol and formaldehyde, reaction between tannin and formaldehyde also includes both methylolation and condensation. Condensation reactions involve the reaction between two methylol groups on adjacent tannin molecules forming an ether linkage, accompanied by the release of water [98,99]. Generally, condensed tannins rather than hydrolysable tannins are used in adhesive applications due to the decreased reactivity of hydrolysable tannins towards formaldehyde [51–53].

The temperature at which tannin is extracted affects the reactivity of bark tannin, while the effect extent depends on bark species and extraction solvents. For barks of southern pine, sweetgum, white oak, red oak and yellow poplar, high temperature extraction in aqueous NaOH results in extractives of high reactivity toward formaldehyde [100]. For spruce bark tannin extracted at 90 °C or 130 °C in water, higher temperature led to a higher tannin yield but lower reactivity towards formaldehyde. Tannins extracted in aqueous urea solution at a higher temperature showed increased reactivity toward formaldehyde [90]. However, the reactivity of tannin extracted at lower temperature can be improved by adjusting the pH level of extracting solution [65,100]. The reactivity to formaldehyde of pine tannins extracted in water in the presence of NaOH, Na_2CO_3, $NaHCO_3$ and Na_2SO_3 was found to increase with increased pH. The use of tannin as a formaldehyde scavenger has been reported by many researchers [66,103].

Tannin based resins can be formulated in several ways. The most common way for tannin based resin preparation involves mixing aqueous tannin with hardeners such as paraformaldehyde, hexamethylenetetramine, tris(hydroxylmethyl) nitromethane, glyoxal or polymeric 4,4′ diphenylmethane diisocyanate (pMDI). Then the pH of the mixture is adjusted to around 10 as alkaline conditions are necessary for the hardeners to decompose into formaldehyde [104–106]. The adhesive properties are dependent on Stiasny number of tannin. A minimum Stiasny number of 65% is essential to produce a high quality adhesive [107]. The reactivity of hardeners towards tannin is dependent on bark species. Kim et al. [104] studied the reactivity of different tannins to different hardeners, paraformaldehyde was found more reactive with wattle tannin than hexamethylenetetramine or tris (hydroxylmethyl)nitromethane, while hexamethylene-tetramine exhibited the highest reactivity with pine tannin.

Increasing the amount of hardeners favors the curing process of adhesives. It has been established that tannin based resins are not only suitable for interior and exterior grade plywoods that meet the European standards EN 314-1 and EN 314-2:1993 based on dry tests, cold water and boiling water tests, they also have low free formaldehyde emissions of the E_1 level according to the European

standard EN-120 [66]. For instance, a tannin–paraformaldehyde adhesive in which tannins were extracted from *A. mangium* bark by water at 75 °C was found to be suitable for interior grade application in terms of bonding strength [55]. Furthermore, the addition of catalysts such as bivalent metallic ions can improve the curing of tannin adhesives (8.2 parts paraformaldehyde as hardener in 100 parts 57.6% aqueous wattle tannin) by shortening press time and reducing press temperature. For example, zinc acetate addition to wattle tannin adhesives in the gluing of exterior grade particleboard was found to decrease press temperature from 130–150 °C to 130 °C [108].

Besides tannin-hardener type adhesive, tannin adhesives can also be prepared through the fortification of synthetic resins such as urea–formaldehyde (UF), PF, resorcinol–formaldehyde (RF) resins, or diisocyanate [109]. The copolymerization and curing of these adhesives is based on condensation reactions between tannin and the methylol groups in the synthetic resin [86]. PF resole-fortified *A. mangium* bark-derived tannin–paraformaldehyde resins (tannin:PF:paraformaldehyde = 90 wt%:10 wt%:3 wt%) meet the requirements for both interior and exterior grade applications. [55]. The quality of adhesives prepared from extracted polyphenolics is dependent on bark species and extraction parameters [78]. Pine bark tannins cannot be used directly for industrial adhesives as they are relatively unstable, and cross-linking is limited due to their high molecular weights, and the incorporation of impurities during the extraction. The high reactivity of some pine bark tannins towards formaldehyde deteriorates the properties of the resulting resin. Thus, it is preferable to react pine bark tannins with low molecular weight resole resins with high methylol contents. Copolymerization of *P. pinaster* bark tannins with high-methylol resole yields a resin that is superior to commercial PF resin for the manufacture of weather and boil proof (WBP) plywood boards. In this case, the amount of soda used to dissolve tannins prior to copolymerization is the most important variable and lower amounts of soda led to better results [110,111]. Hoong et al. [66] reported a tannin adhesive fortified with PF resin (40% solids content), in which the pine bark tannin was extracted in aqueous sodium sulfite and sodium carbonate (100:600:2:0.5) at 75 °C for 3 h. Press times and formaldehyde emissions of three-layer tropical hardwood plywood glued by the fortified tannin adhesive were reduced, while the shear strength still met the minimum requirements of EN-314-1 and EN-314-2:1993 for interior and exterior application, respectively. For maritime pine bark extractives obtained in 1% NaOH extraction at 100 °C for 30 min, the incorporation of tannin solution into PF resin did not adversely affect the physical properties of the resin, and the bonding strength was comparable to that of the pure PF resin [95]. PF resole fortified with *P. pinaster* bark tannin (extracted in aqueous NaOH) was successfully used in bonding *E. globulus* veneer to plywood. It showed the following advantages compared with the traditional PF resole: (1) shorter press time and (2) higher veneer moisture content tolerance. It also exhibited good spreading and satisfactory bonding even with a wood containing high levels of adhesive-repellent substances [93]. Grigoriou [109] researched pine bark (*P. halepensis* Mill) tannin based adhesive fortified with pMDI. In this study, pine bark tannin extracted in water at 80 °C was used as primary adhesive component for exterior grade particleboards. The viscosity of the tannin was reduced by adding 15% ethanol (on extractives solids) with stirring and heating. PMDI and paraformaldehyde were used as the fortifier and hardener, respectively. Then the tannin–pMDI–paraformaldehyde adhesive was sprayed onto wood chips for particleboard production. The results showed pMDI addition improved both strength and swelling properties of the particleboards. When the adhesive formulation contains pMDI in amounts of 20% and 30% based on solid resins, wet bonding strength of the produced particleboards met the requirements of the standard (EN 312 part 5), and a tannin-pMDI mixture with a ratio of 70:30 (w/w) appeared to be most promising in terms of the board's

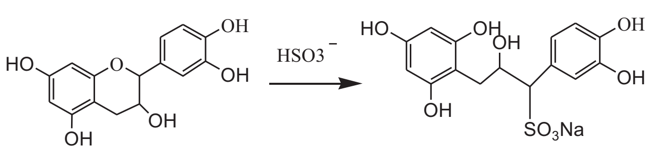


Fig. 3. Sulphitation of tannin .
source: modified from Pizzi [89]

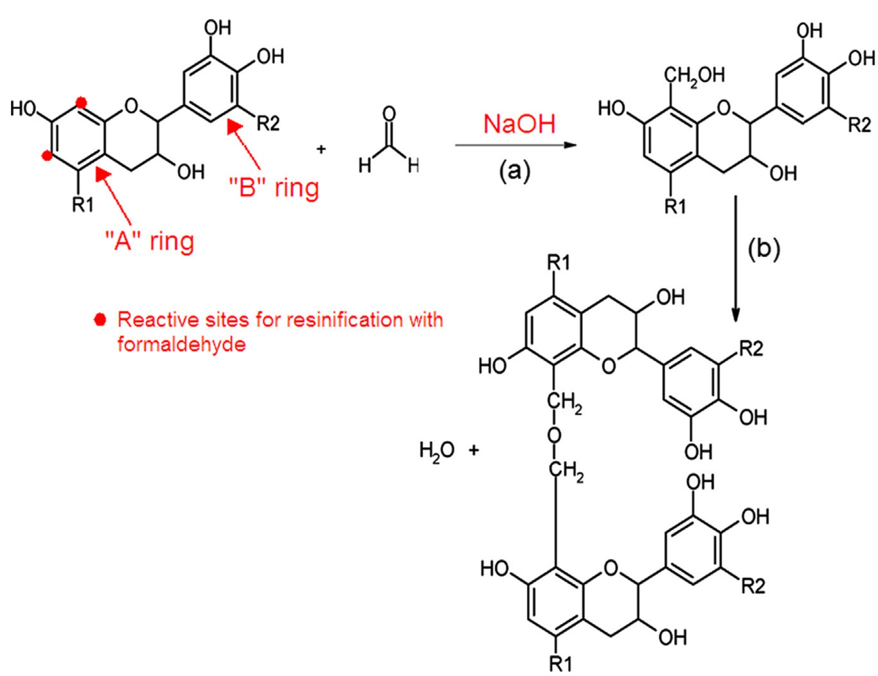


Fig. 4. (a) Methylolation reaction; (b) condensation reaction of flavonoid units in Mimosa tannin during the formation of Mimosa tannin–formaldehyde resin .
source: (modified from [101,102])

weather resistance. In addition, the thickness swell of particleboard bonded with this mixture was lower than that of particleboard bonded with pure bark extractive or pure pMDI adhesives.

Similar to tannin adhesives fortified with synthetic resin, tannin is also added into synthetic resins for fortification [112]. The effects of tannin were found to strongly depend on resin type and the solvent used for tannin extraction. For instance, the chemical curing process of resorcinol–formaldehyde (RF) resin was retarded when adding 10 or 15 parts methanol soluble extractives from *A. mangium*. However, the addition of water soluble extractives increase the gelation rate of PF resins [113], and speed up UF resin curing process, improve the water resistance of particleboard and reduce the formaldehyde emissions [114]. The addition of tannin to phenol–urea–formaldehyde (PUF) resins has been found to lower resin curing temperature. DSC analysis indicates that the addition of *P. pinaster* bark tannin (extracted by aqueous NaOH at 90 °C for 30 min) made the mixed resin chemically curable at the temperature range of 75–85 °C. Also, medium density fiberboard (MDF) bonded with a PUF resin with a 29% tannin content met the European Standard EN 622-5 exterior grade requirements, while the thickness swell of MDF glued with this tannin-modified PUF adhesive was only half of that of MDF glued with commercial resins [112].

Another type of tannin-based adhesive can be produced by substituting tannin for phenol in the PF resin synthesis. Tannin–phenol–formaldehyde resin in which 60 wt % of the phenol was replaced with tannin was found to cure at a lower temperature. PF resin with up to 50% of phenol substituted by tannins from *P. pinaster* bark met the correspond standards for plywood adhesives [110]. However, to synthesize tannin–phenol–formaldehyde resin with a high phenol substitution level is generally challenging due to the too high or low reactivity of bark tannins. One approach to overcome this problem is to phenolate tannin. In one case, black wattle (*A. mearnsii*) tannin was phenolated in the presence of an acid catalyst, then the phenolated tannin was used for synthesize PF resins with 33% replacement of phenol and the resulting phenolated tannin–phenol–formaldehyde (PTPF) resin was used as adhesive for plywood production. Plywoods glued with PTPF adhesive had much better strengths and wood failure than those of tannin–formaldehyde adhesives, which comparable to those of plywood glued with commercial PF adhesives [115]. It was however proposed that pine bark tannin has greater potential to replace more valuable chemicals (such as resorcinol) rather than phenol due to the high cost associated with bark tannin extraction [116].

The fourth type of tannin adhesive refers to polyflavonoid tannin self-condensation without any hardeners [117]. For fast-reacting tannins, such as procyanidins, condensation reactions could be catalyzed by the lignocellulosic substrate to which the resin is applied, resulting in enough strength to satisfy the relevant standards. For slower-reacting tannins like prorobinetinidins and profisdetinidins, a small amount of SiO_2 dissolved in tannin solution at pH of 11–12 could sufficiently catalyze the self-condensation process. The main advantage of this adhesive is that no detectable formaldehyde exists, and the water resistance and wood failure of the glued wood are also acceptable.

In addition to the tannin based adhesives formulated by different approaches as discussed above, various types of formaldehyde-free adhesives have been formulated for industrial wood board/panel production, such as tannin/furfuryl alcohol [118], cornstarch/tannin (tannins as fortifier, 130:13 w/w) resins [119], and tannin/lignin mixture for wood panels of interior applications [120].

Besides tannins, lignin based phenolic adhesives have also gained increasing interest. A number of papers published have shown that lignin has attractive potential for substituting phenol in PF resins. Lignin-based resins are synthesized mainly by simply mixing lignin, phenol and formaldehyde in the PF resin synthesis process. Since 1981 in North America, lignin based PF resins have been reported to be applied in certain mills to manufacture fiberboard, strand board, and structural plywood, principally as a cost-saving measure. As discussed in the section of bark extraction for tannins, aqueous sodium hydroxide has been widely used to effectively extract tannin and lignin from bark. Even though barks have not been used for pulp commercially, several delignification processes including an Acetosolv process of *M. sinensis* bark [121] and an alkaline process of Eucalyptus bark [122] have been reported. Khan et al. [122] cooked Eucalyptus bark in 5 M NaOH at 100 °C for 7 h and recovered lignin by precipitation with 50% H_2SO_4. The recovered lignin, included extractives, was then used as a partial substitute for phenol in PF resole synthesis. It was concluded that up to 50% of the phenol could be substituted. The results showed even though the thermal stability of lignin–phenol–formaldehyde (LPF) resole is lower than that of PF resole, the shear strength of LPF was found to be better than that of PF resole. In addition, the LPF exhibits a lower curing temperature and a higher curing rate.

As a summary, Table 6 lists comparisons of the tannin-based adhesives formulated by different approaches as discussed above.

4.2.2. Tannin-based foams

As is shown in Fig. 2, tannin is natural polyol, containing both aliphatic and aromatic hydroxyl groups, therefore, it can be used as a precursor for polyurethane (PU) foam production. In tannin-based polyurethane foam production, hydroxyl groups on the B-ring of tannin can react with isocyanate. Tannin also acts as a cross-linking agent in addition to hard segments. The oxygen atoms on the A-ring of tannin experience lower electron densities than the oxygen atoms on the B-ring. Therefore the phenolic hydroxyl groups on the A-rings tend not to react with isocyanate, but (+)-catechin can easily react with phenyl isocyanate as illustrated in Fig. 5. Higher tannin contents may result in harder polyurethane foams. It was discovered that catechin or tannin based PU is relatively stable under hydrolytic and aminolytic conditions at room temperature. However, the decomposition rate of catechin and tannin-based urethanes under hydrolysis or aminolysis conditions increases at elevated temperatures [123]. Thus, tannin may be an desirable component of biodegradable polyurethane foams [124].

Apart from tannin PU foam, tannin based rigid foams could be formulated with commercial bark tannin, furfuryl, formaldehyde, acid, water and diethyl ether, among which, water and diethyl ether are the solvent and blowing agent, respectively. Formaldehyde is used to crosslink the tannins, while furfuryl alcohol plays a role as a heat generator and strengthener through both auto-polymerization and its condensation reactions with tannin under acidic conditions [125]. Tannin–formaldehyde–furfuryl (TFF) foams are produced through rapid evaporation of an organic volatile solvent resulting from a mild exothermic reaction, which involves three phases: mechanical mixing, expansion and curing. Mechanical mixing is necessary to obtain a homogeneous and highly viscous mixture of water, formaldehyde, tannin and any additives. The expansion phase starts once the blowing agent and acid catalyst are added to the mixture. The blowing agents (water and diethyl ether) evaporate almost immediately to form foam due to the heat released from self-condensation of tannin with furfuryl alcohol, and then the foam cures. After a very short time, the foam stabilizes through the formation of a tannin/furfuryl network [126]. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analysis has shown that TFF foams contain oligomeric tannin branches and hydroxymethylated furanic chains. These branches and chains are randomly organized to form hetero-

Table 6
Comparisons of the tannin-based adhesives formulated by different approaches.

Types of tannin-based adhesives	Formulation approaches	Advantages	Ref.
Tannin-hardener type adhesive.	Preparation using tannin solution and hardener, with the pH value adjusted to the required level.	Simple preparation procedures, low or none formaldehyde emission, acceptable strength.	[103–108]
Synthetic resin fortified tannin adhesives.	Preparation using tannin solution and fortifier, with the pH value adjusted to the required level.	Ease of application, high spreading, outer door application, absence of detectable free formaldehyde, absence of bleeding and blowouts in the glue line when veneers moisture content is above 8% at high temperatures, improved strength and swelling properties of the bonded boards.	[109–114]
Tannin added synthetic adhesives	Directly mixing of aqueous tannin and synthetic adhesives at room temperature.	Lower curing temperatures, outer door application, low thickness swelling of the MDF boards.	[115,116]
Self-condensed Polyflavonoid tannin without any hardeners.	Fast-reacting tannins, such as procyanidins, catalyzed by the lignocellulosic substrate applied; Slower-reacting tannins like prorobinetinidins and profisdetinidins, with a small amount of SiO_2 dissolved in tannin solution at pH of 11–12.	No formaldehyde emission, acceptable water resistance and strength.	[117]
Lignin based PF resins.	Phenol is substituted by bark lignin during the PF resin synthesis.	Lower curing temperature, higher curing rate, better shear strength, low cost than pure PF resin.	[120]

polymers [127]. The foam is, therefore, an orthotropic material whose density and pore structure are mainly controlled by the amount of blowing agent. A greater amount of blowing agent results in a lower density foam with larger pores [128,129]. Foam density plays a great role in the physical behavior and fire resistance of TFF. The addition of surfactants can increase water absorption without changing foam density [126,130]. An advantage of TFF foam is that the foams collapse under compression and bending [125] as the foam is rather brittle. TFF foam also has comparable properties with PF foams regarding resistance to strong acid, bases, solvents and fire, but a higher affinity for water. In addition, TFF exhibits low thermal conductivity and shock mitigation with compression strengths close to those of phenolic foams.

TFF foam can be further modified by the incorporation of various additives. For instance, the addition of boric or phosphoric acid into TFF foams improved the foam's fire resistance to a great extent [131]. Flexible tannin foams can be prepared by addition of an external (non-reacted) plasticizer. Common TFF foams could reach a stress plateau, but tannin foams without either formaldehyde or glycerol would become very brittle and rigid. Formaldehyde-free tannin/furfuryl alcohol foam presents structure crushing with aging after two months storage. However, the flexibility of glycerol containing formaldehyde-free tannin/furfuryl alcohol foams kept almost constant [132]. Formaldehyde-free tannin–furfuryl alcohol foam could also be polymerized in an acid environment at a temperature of 120–160 °C, resulting in foams of a high homogeneity. By changing the ratio of the components, formaldehyde-free tannin/furfuryl foam with densities of 50–180 kg/m^3 can be formulated. Compared with general formaldehyde reinforced tannin foams, formaldehyde-free light-weight foams exhibit lower mechanical strengths but higher water affinity (the water amount absorbed by the foam could be more than 7 times of the foam weight) [133,134]. In addition, transversely isotropic carbon foam that has extremely low density and surface area, high porosity can be obtained through pyrolysis of tannin based foams in an inert gas atmosphere [135]. It was found that carbonization of tannin–furfuryl foams led to a 3D network in which poly-nuclear aromatic hydrocarbon chains with high molecular weights were covalently linked to furan resin structures. The rearrangement to polyaromatic hydrocarbons of polyflavonoid tannins, constituting aromatic benzene and furan rings and methylene bridges, derived into some complex and 3D structures

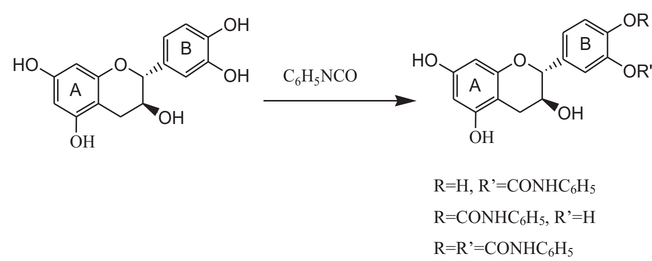


Fig. 5. Reaction of catechin with phenyl isocyanate .
source: (modified from [123])

[136]. The gray carbonized tannin–furfuryl foams are of extremely high absorption and low thermal conductivity. A higher pyrolysis temperature contributes to higher total emissivity, but lower density. A lower density due to thinner and less pore walls would enhance the radiative transfer property for the carbon foams [129,137]. Besides, the carbonized tannin based foams have good electrical conductivity, mechanical strength, coefficient of thermal expansion, permeability and fire resistance, in terms of which, carbonized tannin based foams could compete with commercial vitreous carbon foams [137,138]. Furthermore, TFF carbon foams with high surface areas can be obtained by chemical activation of $ZnCl_2$ or H_3PO_4 treatment [139]. A lower mass ratio of activating agent to tannin resulted in micro-porous carbon foams with a very narrow pore size distribution. With $ZnCl_2$ ratio increasing, the pore size increased. The surface area of the $ZnCl_2$-catalyzed foam could reach to 1875 m^2/g, which is comparable to mirco-porous active carbons.

5. Thermochemical conversion of bark and its applications for materials

5.1. Bark liquefaction

Biomass liquefaction at elevated temperatures in solvents (such as water, phenol, alcohols, acetone, and co-solvents) has been investigated in Japan since the 1970s. Research on thermoconversion of biomass for thermosetting materials like phenolic resins, epoxy resins, polyurethane resins and polyester resins was reviewed by Raquez et al. [101]. In this part, bark phenolysis, liquefaction in

alcohols and other solvents, and their applications in PF resin and PU production are detailed.

5.1.1. Bark phenolysis for PF resins

Phenolysis is a liquefaction process, conducted in phenol with the catalysis of acids at elevated temperature ranging from 80 to 150 °C. Lignin is very susceptible to phenolysis and it is the first component to be emitted from the feedstock during the phenolysis. During phenolysis, decomposed components are apt to undergo extensive condensation under acidic conditions, forming a high yield of char-like solid residue [140]. IR spectroscopy evidenced that the structure of phenolysis residue is very similar to that of cellulose [141]. Phosphoric and sulfuric acids were found to be more effective than hydrochloric acid or oxalic acid in terms of residue ratio after phenolysis [142], and phenolysis catalyzed by sulfuric acid obeys a bimolecular type second-order reaction and Arrhenius law [143]. Due to the abundance of lignin in bark and the susceptibility of lignin to phenolysis [140,144], bark phenolysis has been extensively studied. In bark phenolysis catalyzed with sulfuric acid at atmospheric pressure, acid concentration showed a greater influence than temperature on the chemical composition of the phenolated bark. The primary phenolysis products include phenolic compounds and furans. Pyrolysis-molecular beam mass spectrometer (py-MBMS) spectra show that increasing acid concentration increases the number of phenolic fragments in the phenolyzed bark, and decreases the amount of carbohydrate and unmodified lignin [145]. Also, organic sulfonic acids have been found to completely phenolate some bark. Of even greater interest is that condensation reactions between phenol and the bark components were retarded to a great extent during phenolysis using these organic sulfonic acids [146].

Phenol can be partially replaced by alcohols (particularly methanol and ethanol) during bark phenolysis. High levels of phenol replacement by alcohols were shown to slightly increase the solid residue yield from pine (*Pinus densiflora*) bark phenolysis catalyzed with methanesulfonic acid. A replacement ratio of 20% appears to be optimal for phenolysis according to Hassan's research [147]. In addition to phenolysis at atmospheric pressure, liquefaction of bark in hot compressed phenol without catalysts can be completed in a short time and at conversion rates over 90%. To investigate the phenolysis mechanism of lignin at high temperature, guaiacylglycerol-β-guaiacyl ether (GG) was liquefied at 250 °C by Lin et al. [148]. The results showed that low molecular weight substances were first produced through hemolytic cleavage of the β-O-4 linkage. Then, low molecular weight substances including guaiacol radicals and phenolated products of coniferyl alcohol (diphenylpropenes, phenylcoumaranes, phenylcoumarones and phenylflavanes) would crosslink with phenol to form polymeric products [149]. Coniferyl alcohol radicals consisting of a conjugated double bond in the side chain were found to react extensively with phenol radicals to yield a series of corresponding phenolated products. This reaction pathway may dominate the entire dynamic liquefaction process and contribute to the multiplicity of products. During the liquefaction process, the reaction products obtained from GG liquefaction initially increased with time, then gradually approached an equilibrium distribution. The time needed to reach the equilibrium depended on reaction temperature. While the molecular weight distribution at the equilibrium state was dominated by the ratio of phenol to GG, self-condensation of the intermediates from liquefaction gave rise to multi-condensed products with molecular weights ranging from several hundreds to several thousands. A decrease in phenol/GG ratio led to an increase in the amount and molecular

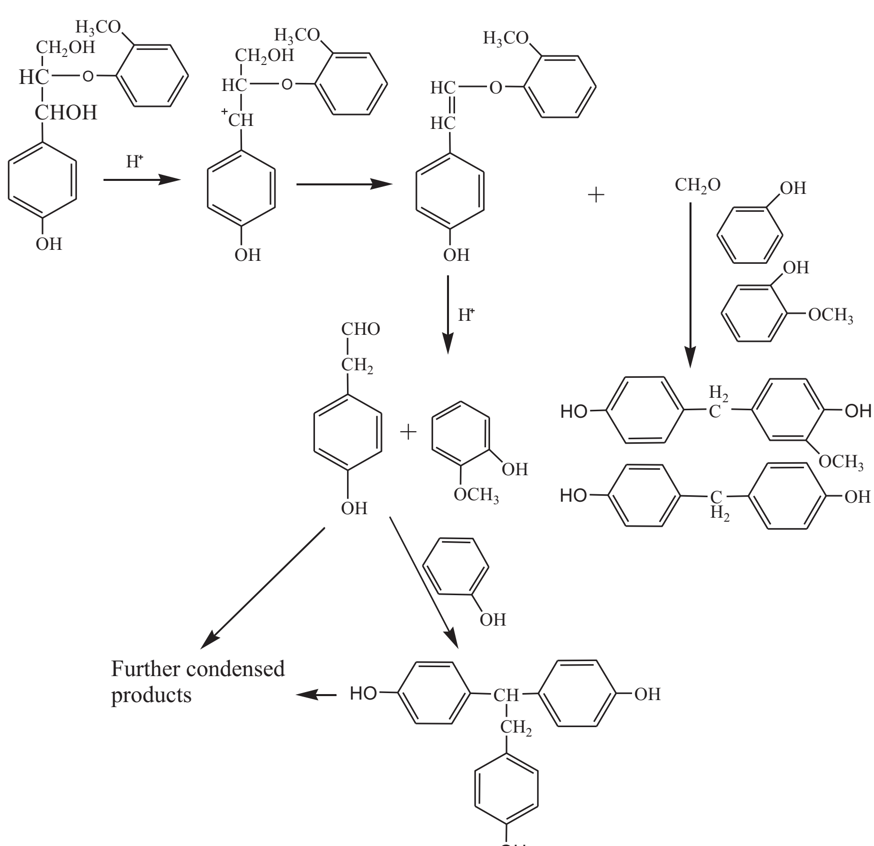


Fig. 6. Scheme for the possible reaction pathway of GG with phenol catalyzed by sulfuric acid .
source: (modified from Lin [154])

with those of commercial Novolac moldings [154].

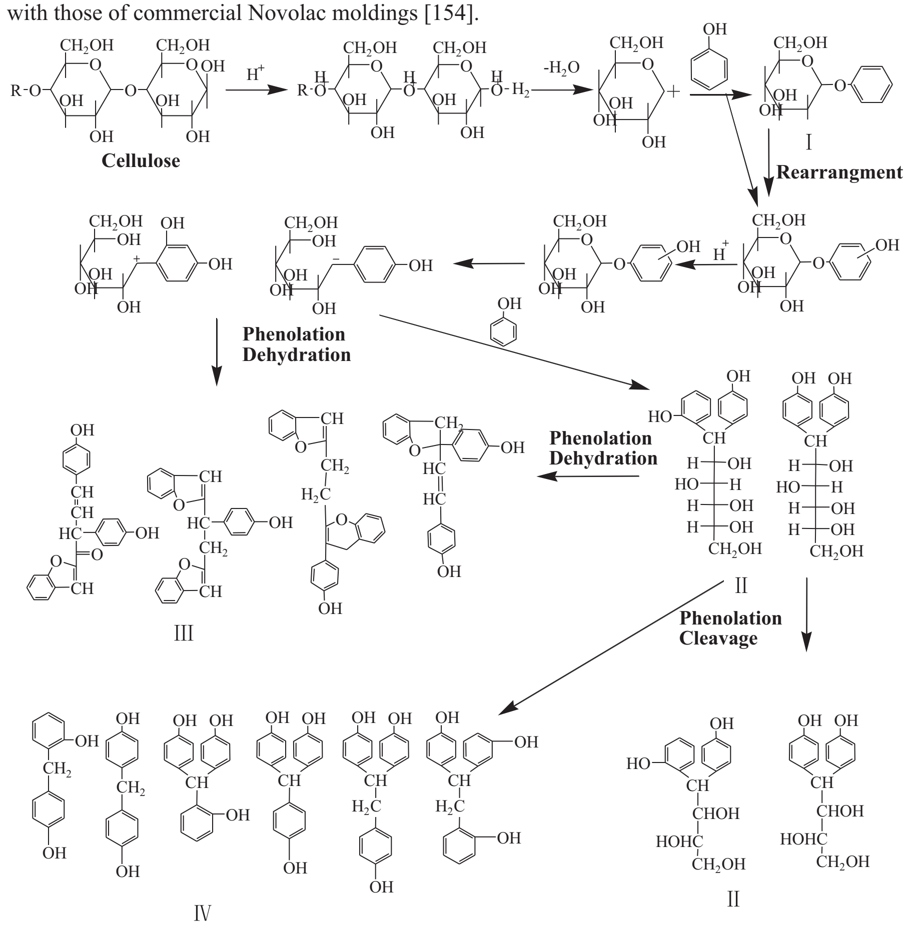


Fig. 7. A proposed cellulose phenolysis pathway with acid catalyst .
source: (modified from Lin [153])

weights of multicondensed products, suggesting that phenol plays a key role in retarding self-condensation of the reactive intermediates [150]. As shown in Fig. 6, it can be concluded that the phenolysis pathways of lignin with sulfuric acid catalyst involves decomposition, phenolation and recondensation reactions. In addition, as shown in Fig. 7 the phenolysis process for lignocellulosic biomass may also involve degradation and dehydration of glucose, condensation between phenol and dehydrated glucose, phenolation and cleavage, and the reactions between the degraded products with phenol [151,152]. For cellobiose phenolated with the sulfuric acid, four types of compounds including about 17 main compounds were detected after phenolysis [153].

Phenolated bark has been mainly utilized for PF resins. It was reported that the global production and consumption of PF resins in 2009 was approximately 3.0 Mt, with an average annual growth of 3.9% from 2009 to 2014, and a projected growth rate of 2.9% from 2014 to 2019 [155]. In North America, PF resins account for about 32% of the total solid resins used in relation to 59% of amino resins and 9% other binders like isocyanates [156], The North America's PF resin production industry is valued as much as $2.3 billion [155]. As phenol is the most expensive material used in PF resin synthesis, even partial substitution of phenol would greatly benefit the PF resin industry. As shown in Fig. 8, both phenolic novolac and resole resins could be synthesized using the phenolated bark.

There are three pathways for novolac resin production using phenolated bark. The first one involves direct condensation of phenolated bark, bark residue and formaldehyde with an acid catalyst, among which bark residue plays a role of filler in molding.

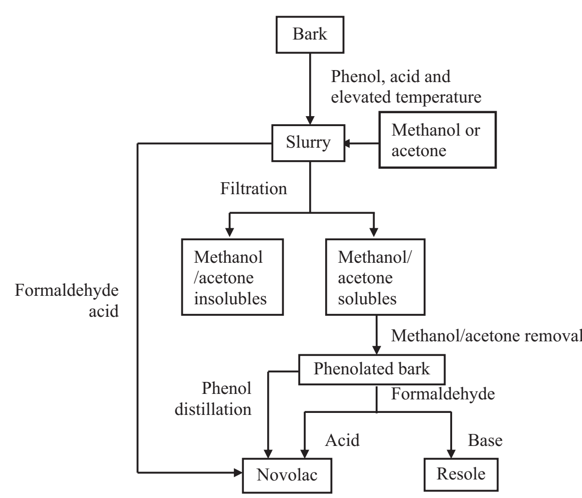


Fig. 8. A general process of bark phenolysis for Novolac or Resole resins

The other two pathways include the dissolution of reaction slurry-alike product after phenolysis in an organic solvent (methanol or acetone), the insoluble and soluble fractions are separated by filtration. The soluble fraction was evaporated to remove solvents and free phenol, while the resulted residual phenolated bark was directly applied as Novolac [157]. The third pathway for phenolated bark based Novolac synthesis is the most popular one, which mainly involves the condensation between phenolated

bark (including the free phenol) and formaldehyde. This pathway differs from Pathway-2 in that removal of free phenol is not needed.

Compared with phenolated bark based Novolac resin, resole preparation from phenolated bark is much easier as shown in Fig. 8, i.e., the phenolated bark is reacted together with a basic catalyst and formaldehyde for PF resole production. It is worth noting that enough amount of base is needed to neutralize the acidic phenolated bark first and then to catalyze the resole synthesis. Zhao et al. [159] phenolated lodgepole pine (*Pinus contorta* Dougl.) bark at the bark/phenol ratio of 1:3(w/w) using sulfuric acid as the catalyst (3% based on phenol weight) at 150 °C for 120 min. The phenolated bark was then condensed with formaldehyde and NaOH added by two stages: in the first stage 1/3 of the total NaOH was added and the temperature was elevated to 65 °C within 30 min and kept at 65 °C for about 10 min, followed by the addition of the remaining 2/3 of NaOH. The mixture was then heated to 85 °C and kept at the temperature for 60 min. Characterizations showed that compared with the commercial PF Resole, the resulted phenolated bark PF resins (PBPFs) displayed higher average molecular weights, polydispersity indices, viscosity and shorter gel times. Plywood samples bonded with PBPF display higher or comparable strengths and wood failures to those glued with commercial PF resins, and some PBPFs show even higher wet bonding strengths than pure PF resins. Bark species could affect the resole properties, e.g., the phenolated China fir bark-based resole displayed higher viscosity than Taiwan acacia bark-based resole. In terms of thermosetting characteristics, phenolated Taiwan acacia bark-based resole exhibited higher exothermic peak temperature and onset temperatures as well as a larger quantity of exothermic heat than the China fir bark-based resole [160]. Pretreatment like tannin extraction can also affect bark phenolysis and its derived resoles. Crude bark was demonstrated to be phenolated more readily than tannin-free bark. Plywood glued with phenolated crude bark based resole showed a larger wood failure percentage and higher shear strength than those glued with phenolated tannin-free bark based Resole [161]. For the effects of catalysts, resoles prepared from H_2SO_4 catalyzed phenolated bark had higher viscosity. While resoles synthesized from HCl catalyzed phenolated bark showed a higher peak temperature, a lager exothermic peak, and a larger quantity of exothermic heat during thermosetting. Particle-board glued with H_2SO_4 catalyzed phenolated Taiwan acacia bark based resole (solid content of 43.0%, viscosity of 350 cP and gel time of 15.4 min) demonstrated better properties than those glued with other adhesives, with satisfactory wet static bending strength and IB [160].

5.1.2. Solvolytic liquefaction of bark for polyurethane form production

Different from the above described phenolysis, solvolytic liquefaction of biomass using low boiling point solvents such as water, alcohols (methanol and ethanol) or their mixtures in sub/supercritical conditions (250–350 °C) has proven to be an effective way to liquefy lignocellulosic materials. Owing to the low dielectric constants of alcohols, alcohols are expected to readily dissolve the relatively high molecular weight products deriving from cellulose, hemicellulose and lignin depolymerization/degradation [162], hence reducing char formation. Reaction temperature is very important for biomass liquefaction conducted in alcohol solvents [163], and supercritical conditions were found to be more effective than subcritical condition with respect to biomass conversion. Polyhydric alcohols such as ethylene glycol (EG) [164] and glycerol [165] have been found to be highly active in liquefying lignocellulosic biomass into polyols, which is essential for bio-based polyurethane (PU) foams. The lignin in wood processed in acidified ethylene glycol was converted into N,N-dimethylformamide (DMF)-soluble compounds in the initial stages of wood liquefaction, while cellulose was gradually converted into DMF-soluble compounds. The relatively slow cellulose conversion rate determined the whole-wood liquefaction rate [164]. During the liquefaction, condensation reaction can also occur, leading to the formation of char or solid residues. The condensation reactions occur commonly during the biomass liquefaction, it tends to be less severe during the liquefaction of the individual components (e.g. cellulose powder, lignin or alkali lignin) indicating that condensation reactions occur readily between cellulose- and lignin-derivatived intermediates [166].

Simple glycols such as ethylene glycol or propylene glycol have been shown to favor bark liquefaction and the use of glycerol–glycol mixture (e.g., glycerol 10%) showed synergistic effects on bark liquefaction [167]. It has also been reported that a glycerol-containing polyethylene glycol (PEG) system produced a high yield of liquid products of stable hydroxyl values as well as a lower yield of solid residues [34].

Bio-oils from lignocellulosic biomass liquefaction in polyhydric alcohols could be used for the production/synthesis of resins [168,169], polyesters [170], and polyurethanes (PU) etc. The PU that is extensively used in heat-insulation, packaging, structure, flotation and load bearing materials is generally prepared through the polymerization between isocyanates and petroleum-derived polyols. Currently, the annual market for PU in North America is about 2.8 million tons and the raw materials for preparing PU foams are obtained almost entirely from fossil resources [171]. Bio-based polyols have attracted a great deal of attention. It was believed that natural polymers containing two or more hydroxyl groups in the main chain could be potential polyol sources for PU preparation [172,173]. So far, bio-polyols from lignocellulosic resources such as dried distillers grain [171], wheat straw [174,175], corn bran [176], lignin [177], and cellulose [178] have been demonstrated as potentially viable feedstocks for bio-PU production.

Bark is also a potential source of polyol feedstock for bio-PU production as it is rich in both tannin and lignin, along with cellulose and hemicellulose, which are all natural polyols. So far, bark has been utilized in PU production through two pathways. The first pathway involves bark liquefaction, while the other pathway only involves direct mixing of bark powders with other precursors. The first pathway was demonstrated in a report to produce highly resilient (HR) polyurethane foams (PUFs) suitable for car-seat cushions. The bark of *A. mearnsii* (BK) and cornstarch (CS) were liquefied in a solvent mixture consisting of poly(propylene glycol) (PPG), glycerol, and sulfuric acid with weight fractions of 94/5/1 at 150 °C [167]. The liquefied products were suspended in polyethylene glycol (PEG) and stirred at 80 °C for 5.5 h before cooling down to room temperature. Then surfactant, catalyst, cross-linking agent, and diisocyanate were added to the suspension and stirred at 700 rpm to yield a PU foam. The bark and its derivatives were found to play the role of cross-linking agents in the PU foams. Employing mixtures of PEG and glycerol made the liquefied bark fraction a slightly higher hydroxyl number than that obtained by using PEG alone, indicating that mixture solvent is superior to a mono solvent for bark based PUF production [167,179]. The addition of glycerol or PEG to the solvent mixture used in the liquefaction of mountain pine beetle (*Dendroctonus ponderosae hopkins*) infested lodgepole pine (*P. contorta Dougl.*) bark with sulfuric acid catalyst at 150 °C, was found to remarkably reduce the residue ratio as well as the lignin content in the residue. PU foams produced from PEG–glycerol liquefied barks have a higher density than that made from mono-solvent liquefied barks, even though he compress mechanical properties, gel

content, thermal stability and cell structure of the bark based PU foams were influenced by both ratio of bark and pMDI and liquefaction solvent [180].

The other pathway for bark-based PU production is to directly mix fine bark powder with isocyanate and some other additives. In a process patented in 1977, ground bark (100 mesh) was blended with pMDI, a blowing agent (i.e. water), surfactant, and catalyst to produce PU foam [181,182]. In the process by Ge et al. [182], oven dried *A. mearnsii* Dewild bark powder was suspended in a polyether polyol at room temperature for one to two days. Then dibutyltin dilaurate (catalyst), silicone oil and water (blowing agent) were added to the polyether–polyol slurry and stirred until uniform. Then, MDI was added to the mixture and transferred into a molder, heated to 60 °C with a 15 min hold before cooling down to room temperature. After 1 h at room temperature, the mold was removed and the foam was left at room temperature for seven days. To increase the amount of bark or addition of water was found to decrease density of PUF, but the decrease in density could be inhibited by the addition of tannin. Increased water content generally resulted in higher thermal conductivity of the PUF. Conversely, increased bark content led to lower thermal conductivity [183].

5.2. Bark pyrolysis and pyrolysis oil-based resins

Pyrolysis is a thermal decomposition process, conducted in an inert (no oxygen) atmosphere, yielding charcoal, pyrolysis oils, water and gaseous products. The product distributions depend on feedstock properties such as biomass species, moisture, and particle size, as well as process parameters including reaction temperature, vapor residence time, heating rate and reactor type, etc. [184–186]. Pyrolysis is generally divided into three categories: slow pyrolysis, fast pyrolysis and vacuum pyrolysis based on the conditions under which the pyrolysis occurs.

Slow pyrolysis yields a large proportion of solid charcoal, while both fast and vacuum pyrolysis produce more liquid bio-oil. Fast pyrolysis is operated usually between 400 and 600 °C with rapid heating rates and short vapor residence times [187,188]. As fast pyrolysis bio-oil is produced in a very short time, the components substances comprising the bio-oil are not in thermodynamic equilibrium. These chemical components, therefore, tend to react in the direction of thermodynamic equilibrium during storage via reactions such as condensation between aldehydes and aromatic units, and the polymerization of aryl-vinyl, aryl-allyl, and aryl-crontonyl fragments in addition to acetal formation between the carbonyl and alcohol groups. These reactions lead to great increases in the viscosity and molecular weight of the bio-oils [189–192]. The addition of alcohols, especially methanol, has been found to be effective in improving the homogeneity of pyrolysis oil, decreasing the viscosity and density, reducing the flash point and increasing the heating value of pyrolysis oil [193].

Vacuum pyrolysis is a special type of fast pyrolysis, which is conducted at very low pressure. Bark vacuum pyrolysis oil is a dark, viscous and oily product that visually appears to be homogeneous. The physicochemical and colloidal properties of this oil are similar to those of fast pyrolysis oil [193–195]. Microscopic tests have shown that solid particles, structured materials and droplets exist in vacuum pyrolysis oil, which tend to increase bio-oil viscosity, causing non-Newtonian flow behavior, and impairing combustion properties. Bark vacuum pyrolysis oil can be separated into water soluble and water insoluble fractions. The water soluble fraction derive from holocellulose and are highly polarity, while the water insolubles stemming mainly from lignin have lower polarity. TGA analysis indicates that, due to the presence of lignin derivatives, the water-insoluble compounds decomposed at a relatively higher temperature than the whole bio-oil and water-soluble compounds [196,197].Bark vacuum pyrolysis oil as a whole is unstable, and it's viscosity increases significantly in the first 60 days of storage at room temperature, but afterwards the viscosity remains almost constant [198].

Currently the world energy is provided dominantly through the combustion of fossil fuels. However, due to the declining fossil reservation, increased energy demand/consumption and the concerns over greenhouse gas emissions, searching for alternative and sustainable energy sources attracts wide attention. Pyrolysis has been assessed as an alternative biofuel production process since 1980s [199,200], and is the only industrially realized technology for biomass liquefaction. Bark pyrolysis can yield more than 50% of bio-oil, and as bark contains a comparatively high content of extractives, bark pyrolysis oil's heating value is higher than wood pyrolysis oil's [8,201]. Compared with crude bark or bark pellet, bark pyrolysis bio-oil can be easily transported and stored due to its increased energy density. Meanwhile, pyrolysis bio-oil as a renewable fuel is considered carbon-neutral, and it contains negligible sulfur and nitrogen, which makes combustion of bark pyrolysis oil emits almost no SO_2 and NO_x compared with fossil fuels. Combustion test demonstrated that pyrolysis bio-oil can be burnt efficiently in conventional or modified burners [200]. For example, vacuum pyrolysis bio-oil from softwood bark (70 wt% fir, 28 wt% white spruce, 2 wt% larch) with a heating value of 31 MJ/Kg was tested as a valuable gas turbine fuel [202]. The advantages of using pyrolysis bio-oil as fuel may be summarized as follows: low production cost, positive CO_2-balance, possibility to decouple solid biofuel handling from utilization (reduced capital and operation costs in utilization), easy storability and transportability, high-energy density [199]. However, like common bio-oils, bark bio-oil has some poor properties, including two phase nature, high contents of oxygen, water, solids and ash, high viscosity and surface tension, chemical and thermal instability, low pH values (corrosive) [203]. Further upgrading such as steam reforming and catalytic upgrading is essential [202].

Thus, valorizing pyrolysis oil for the production of chemicals seems to be more economical than using it as a fuel. Many patents have been filed on the recovery of phenolic compounds from pyrolysis oil, as well as the application of pyrolytic phenolic compounds in PF resole production [204–207]. Steam distillation pyrolysis oil was found to be efficient in separating light oil, rich in phenolic compounds, from heavy oil at a low temperature [208]. Amen-Chen et al. [209–211] pyrolysed softwood bark at 505 °C at a total pressure of 18 kPa, then used the bio-oil in synthesizing PF resole by partially substituting phenol. PF resole in which up to 25 wt% of the phenol was replaced by softwood bark pyrolysis oil was found to cure with very similar kinetics to pure PF resoles. But when the phenol substitution ratio was increased to 50 wt%, the resulting PF resole showed slower cure kinetics and a lower condensation reaction rate compared with the pure PF resole. The curing process could be enhanced by the addition of propylene carbonate in the range of 0.5–1.5% on a resin solid basis. An unfortunate side effect of increasing phenol substitution with pyrolysis oil is the reduction of the resulting resin's thermal resistance.

For oriented strand boards (OSB) glued with a PF resin in which 25 wt% or 35 wt% of phenol was substituted by softwood bark pyrolysis oil, their mechanical properties (MOR, MOE and IB) and physical thickness swelling exceeded the minimum requirements of CSA 0437-1993 in both dry and wet (2 h boiling) tests [212]. Homogeneous OSB bonded with PF resoles with different phenol substitution levels (25 to 50%) exhibited comparable MOR, MOE and IB to those of OSB glued with a commercial PF resole. Three layer OSB whose surface and core layer were glued with PF Resoles in which 50% and 25% phenol was respectively replaced by bark pyrolysis oil exhibited mechanical properties meeting the

Canadian standards CSA O437.0-1993 for OSB products [206]. It is interesting that fractionation of pyrolysis oil does not further improve the properties of bio-oil based PF resins [213]. In addition to being used as a phenol substitute in PF resin synthesis, bark pyrolysis oil can be also used as a PF resin substitute directly for wood modification. The impregnation of PF resins and bark pyrolysis oils into wood blocks improves decay resistance without negatively impacting wood mechanical properties [214,215].

In addition, pyrolysis oil can be blended with isocyanate to produce adhesives. The chemical reactions between pMDI and softwood bark pyrolysis oil occur below 100 °C. The peak temperature of reaction increases with the decreased bio-oil content in bio-oil/pMDI blends. The highest rate of formation of the chemical linkages between bio-oil and pMDI was obtained at bio-oil contents between 30 and 40% [216]. All particleboard properties excluding thickness swell did not show significant difference among the pMDI/bio-oil blends with bio-oil contents of 30%, 35% and 40%. When the bio-oil fraction in particleboard adhesives (bio-oil/pMDI blends) is 40%, the bonded particleboard still meet the requirements for interior grade applications without reduced the physical (thickness swell) and mechanical properties (IB, MOE and MOR) [217]. According to another recent study by Mao et al. [218], an adhesive blend with a pMDI/bio-oil ratio of 3:1 resulted in bonding properties comparable to those of pure pMDI resin, and the addition of acetone to the pMDI/bio-oil blend was found to decrease the resin's viscosity by 67%, a significant advantage in applying the resin to wood strands with a sprayer.

6. Summary and perspectives on chemicals and materials production from tree barks

The annual bark yield in Canada is as much as 17 million m^3. Currently, more than half of the bark is incinerated or landfilled and the remainder of the bark is mainly used as a cheap source of energy in saw/pulp mills. Both bark incineration and landfilling can lead to environmental problems. Due to the abundance of ash in bark and the low sintering point of bark ash (lower than that of wood ash), the combustion of bark can lead to fouling which would damage the combustors. As a result, bark is not an ideal fuel for direct energy production. It is also not a particularly promising feedstock for secondary fuel production. Bark comprises a large fraction of extractives and lignin (up to 50 wt% on a dry basis). These are aromatic chemicals which retard both the hydrolysis and fermentation reactions necessary for ethanol production. Therefore, the utilization of bark for chemicals and materials through extraction or thermochemical conversion rather than as a direct energy source or through bio-conversion for bio-ethanol production is more feasible and economically advantageous.

Over the past few decades, much research has been conducted to investigate the production of value added products from bark. However, the only commercial product may be only Acacia bark tannin. Direct utilization of bark for wooden panels would be a good pathway if the mechanical properties and water resistance of bark based wooden panels could be further improved. Another challenge in bark valorization is the difference in the chemical composition of bark among tree species, which makes the development of a universal process for all bark utilization almost impossible. The tannins used in tannin-based resins, for example, are mainly extracted from the barks of spruce, pine, wattle and eucalyptus, etc. In many cases, alkaline solutions are utilized in bark extraction to achieve a high extractives yield. The resulting extractives include some tannin, but also include larger quantities of lignin and holocellulose derivatives. The mechanical properties of alkaline extractives based adhesives can meet some mechanical and physical standards. Studies on tannin-based PU foam production have lasted for a long time, but not been commercialized yet. Apart from tannin PU foam, TFF foams are new materials mainly researched by Dr. Antonio Pizzi's Group. TFF foams collapse under compression and bending and have comparable properties with PF foams in terms of the resistance to strong acid, bases, solvents and fire, and compression strengths, although TFF has higher affinity to water but low thermal conductivity and shock mitigation. Moreover, gray carbonized TFF is of extremely high absorption and low thermal conductivity, making it a promising thermal insulation material. As such, once the TFF production process becomes mature, commercialization of bark-derived tannin would be economically feasible.

Thermochemical conversion processes, especially bark phenolysis and solvolytic liquefaction, seem to be promising technologies for the production of bio-based PF resole resins and polyurethane foams. It has been demonstrated that the curing and mechanical properties of bark-based PF resole resins and PUFs are comparable or even better than commercial PF resoles/PUFs. However, bark-based PF resole resins and PUFs generally exhibited inferior water resistance, and the highest phenol substitution ratio achieved was only approx. 30%. Bark pyrolysis processes can produce large yields of bio-oil, but like bio-oils derived from other biomass, bark pyrolysis bio-oil has some poor properties, including the tendency to separate into water soluble and insoluble phases, high contents of oxygen, water, solids and ash, high viscosity and surface tension, chemical and thermal instability, low pH values, as well as poor ignition and combustion properties. Even though the heating value of bark pyrolysis bio-oil is higher than that of wood pyrolysis bio-oil, it is still only about half of the heating value of commercial fuels. To improve the properties of bark pyrolysis oil sufficiently to meet the engine fuel requirements, further energy-consuming upgrading steps such as steam reforming or catalytic upgrading are required. Therefore, valorization of bark for chemicals or materials such as foam materials and adhesives is more promising than for fuels, although fractionation and other post-treatment of bark-derived bio-oils are still necessary. Further research is needed to increase bio-oil substitution ratios and to scale up the processes for industrial applications of bark for chemicals and materials.

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